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Dynamic modelling of the fate of DDT in Lake Maggiore: Preliminary results

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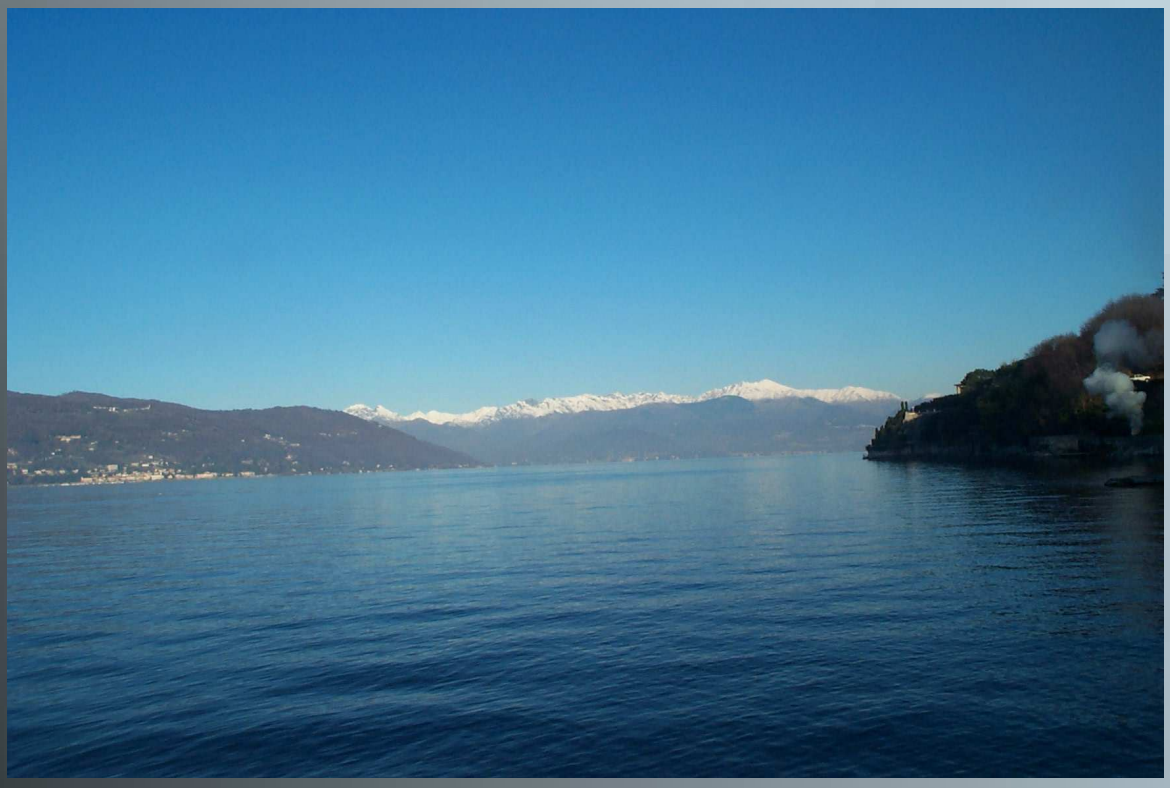

Institute for Environment and Sustainability

2005

EUR 21663 EN

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Directorate-General Joint Research Centre
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EUR 21663 EN
Luxembourg: Office for Official Publications of the European Communities

Printed in Italy

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INTRODUCTION

Release of chemical substances significantly impacts European waters. Impacts are both direct and indirect, through degradation products, acute and/or chronic toxicity, and/or long-term effects via bioaccumulation in aquatic food chains. As the number of substances is large and measures to reduce emission are costly and time demanding, there is a necessary prioritisation of the efforts through risk assessment studies requiring exposure data, which are both scarce and difficult to obtain. This is complicated by the fact that contaminants may reach the aquatic environment and hence biota and sediments, through several routes ranging from atmospheric deposition (airshed), diffuse and/or point sources in the watershed. Furthermore, a contaminant may arrive constantly during the year or in a pulse due to an accidental release or periodically driven by environmental fluctuations.

The role of mathematical models in assessing the fate and effects of contaminants in aquatic ecosystems is continuously increasing, for a recent review see Koelmans *et al*., (2001). Mathematical models, once properly validated, offer the possibilities to simulate process that would not be possible to measure in reality; to forecast the results of different plausible scenarios; and to extract information about the global dynamic behaviour of the studied system which would be impossible from any field experiment. However, to develop and validate such as model a considerable amount of experimental data is required.

For these reasons, as a first step, we have developed a model to simulate the fate of DDT family, i.e. pp'DDT, pp'DDD, pp'DDE, op'DDT, op'DDD, op'DDE, in Lake Maggiore. The lake has been extensively studied from the limnological view point (Commission for the Protection of the Italian-Swiss Waters, http://www.cipais.org/, CIPAIS, 1999a; 2000; 2001; 2002a) and also, after that in 1996 very high levels of DDT - beyond the legal limit for several edible fish species- were found, experimental data on DDT exists (CIPAIS, 1999b; 2002b; 2003) for different environmental compartments, e.g. water column, sediments, biota. This increase in DDT concentrations was responsible for the banning in June 1996 of the commercial fishing of some species. The source of the pollution was traced back to a chemical plant (CIPAIS, 1999b), which both produced and discharged DDT over several years into River Marmazza, a tributary of River Toce, which is in turn one of the major affluent of Lake Maggiore.

The model is 0D and consists on a dynamic mass balance that includes a time-variable chemical transport and fate model for calculating DDT concentrations in the water column as well as and in sediments based on Farley *et al*., (1999) model for PCBs in Hudson river and estuarine. An overview of the processes included in the DDT model is represented in fig. 1.

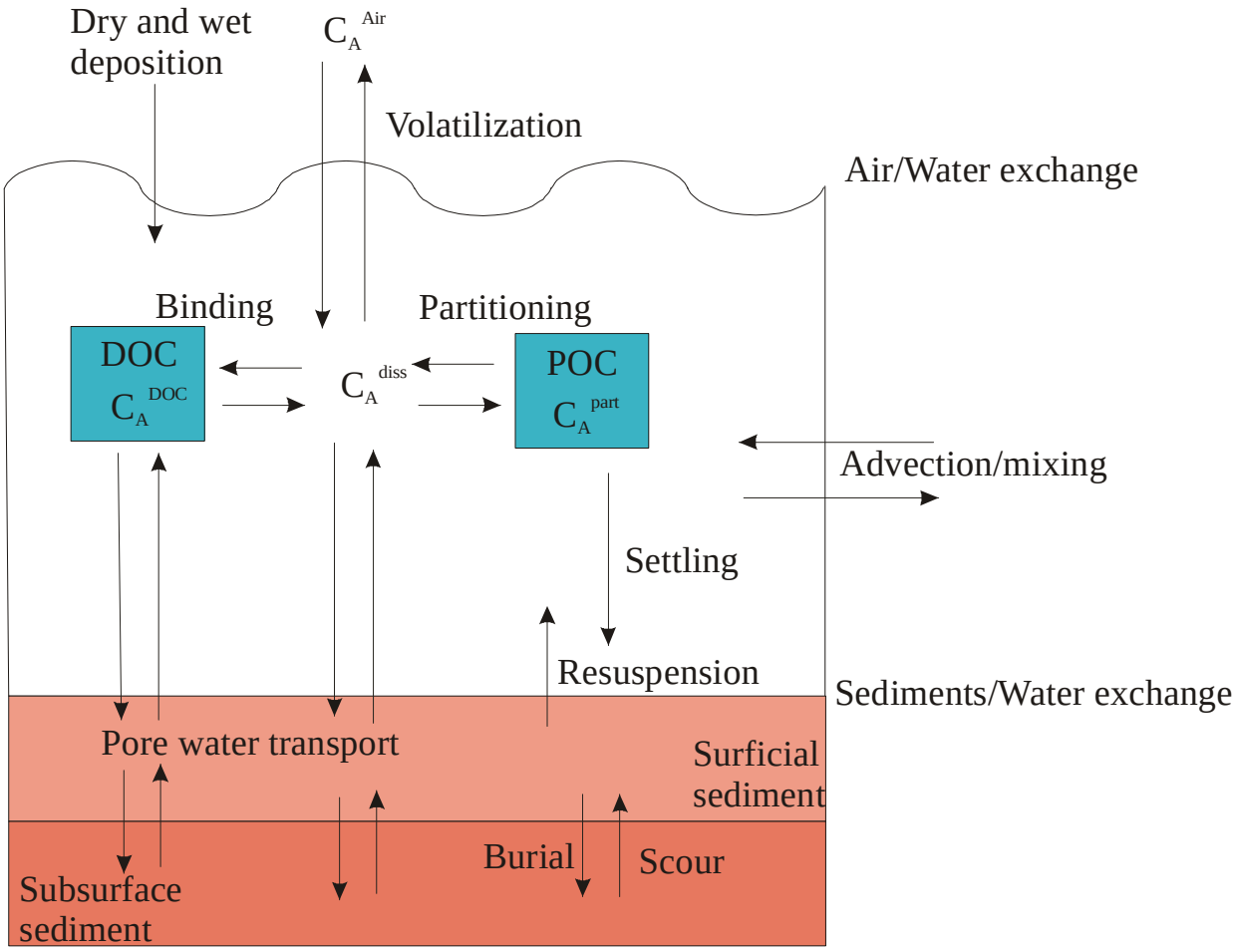

Figure 1. Overview of processes included in the DDT fate model.

FATE AND TRANSPORT OF DDT: MASS BALANCE MODEL

Assuming a well-mixed water column, i.e. a 0D model, underlain by two layers of sediment: active and inactive, see fig.1, and that the sorption reactions are fast compared with the other environmental processes, then the mass balance equations for the different compartments can be written as (Farley *et al*., 1999):

- *Total concentration in the water column*:

$$V\frac{dC_T}{dt} = Q_{in}\cdot C_{in} - Q_{out}\cdot C_T + W_C - w_s\cdot A_s\cdot m\cdot\Gamma + w_u\cdot A_s\cdot m_{sed}\cdot\Gamma_{sed} \quad (1)$$
$$- A_s\cdot F^{W/S} + A_s\cdot F^{A/W} + A_s\cdot F^{dep} - k\cdot V\cdot C^{diss}$$

The first and second term of the *rhs* represent the mass rate of chemical flowing into and out of the system; the third term represents the chemical input rate from external sources, e.g. effluent discharges; the fourth term represents the chemical loss from the water column by settling; the fifth term represents the rate of chemical gain from resuspension; the sixth term represents diffusive exchange between dissolved concentrations in the water column and pore (interstitial) waters; the seventh term represents the transfer of chemical across the air-water interface; the eighth term represents the input by wet and dry deposition; and the last term represents transformation losses from the water column, e.g. by aerobic degradation.

- *Total concentration in the sediments*:

A similar equation can be written for the sediments:

$$V_{sed}\frac{dC_T^{sed}}{dt} = w_s\cdot A_s\cdot m\cdot\Gamma - w_u\cdot A_s\cdot m_{sed}\cdot\Gamma_{sed} - w_b\cdot A_s\cdot m_{sed}\cdot\Gamma_{sed} \quad (2)$$
$$+ A_s\cdot F^{W/S} + A_s\cdot F^{S/S} + A_s\cdot F^{bio} - k_{sed}\cdot V_{sed}\cdot C_{sed}^{diss}$$

The first term of the *rhs* represents the gain of chemical by settling whereas the second and third represent the loss of chemical by resuspension and by burial into deeper sediments, respectively; the fourth and fifth terms represent the diffusive exchange between dissolved chemical with the overlying water and deeper water sediment pore, respectively; the sixth term represents the sediment mixing near the surface due to bioturbation, and the last term represents transformations in the sediment, e.g. anaerobic degradation.

In this case DDT in the water column can be divided into two main parts related to their fates and transport routes: dissolved and particulate, i.e. $C_T = C^{diss} + C^{DOC} + C^{part}$. Particulate bound DDTs are subject to sedimentation and, hence, they will be highly retained by the system than the dissolved phase and will affect directly the benthic ecosystem, whereas dissolved micropollutants (*diss+DOC*) will interact with the pelagic system. Of course, there are always pathways between pelagic and benthic compartments. A general approach to describe the particle affinity is by means of the partition coefficient K_d ($m^3/\mu g$ dw) which is defined as the ratio between the particulate and the dissolved phases as:

$$K_d = \frac{\Gamma}{C^{diss}} \quad (3)$$

whereas C^{diss} is the dissolved concentration (ng/m^3) and Γ(ng/μg) is the ratio between the particulate concentration (C^{part}, ng/m^3) and the suspended particulate matter concentration in mass dry weight per volume (m, μg dw/m^3):

$$\Gamma = \frac{C^{part}}{m} \tag{4}$$

Furthermore, the dissolved phase can be distributed between free chemical and chemical bonded to dissolved organic carbon (*DOC*). Also in this case an equilibrium partitioning relationship it is assumed:

$$K_{DOC} = \frac{C^{DOC} / DOC}{C^{diss}} \tag{5}$$

Concerning the sediments a similar distinction should be made between dissolved (interstitial or porous water) and particulate concentrations. The total concentration of the chemical normalised to the volume of the sediment (ng/m^3) can be expressed as: $C_T^{sed} = C_{sed}^{part} + C_{sed}^{DOC} + C_{sed}^{diss}$. If we define Γ_{sed} (ng/μg dw) as the concentration of the chemical in the sediment then we can write:

$$C_{sed}^{part} = (1-\phi_{sed})\rho_{sed} \cdot \Gamma_{sed} \tag{6}$$

where ϕ_{sed} and ρ_{sed} are the porosity and density of the sediment, respectively. Also in this case

$$C_{sed}^{diss} = \phi \cdot C_{sed}^{\text{int } w} \tag{7}$$

where $C_{sed}^{\text{int } w}$ is the dissolved concentration in the interstitial water.

2.1 Sorptium equilibria

Since sorptium equilibria determines the concentration partitions between the freely-dissolved, DOC bound and particulate phases it is fundamental to have an accurate description of these phenomena in order to simulate correctly the dynamics of a micropollutant. Using Eqs. (3)-(5), it is possible to express the concentration in each phase for the water column, as well as for the sediments, as a function of the total concentration and the equilibrium partition relationships (Farley *et al*., 1999):

$$C^{diss} = \frac{C_T}{\phi + \phi \cdot K_{DOC} \cdot DOC + K_d \cdot m} \tag{8}$$

$$C^{DOC} = \frac{K_{DOC} \cdot DOC \cdot C_T}{\phi + \phi \cdot K_{DOC} \cdot DOC + K_d \cdot m} \tag{9}$$

$$C^{part} = \frac{K_d \cdot m \cdot C_T}{\phi + \phi \cdot K_{DOC} \cdot DOC + K_d \cdot m} \tag{10}$$

where the porosity ϕ in the water is equal to one.

Normally, in fate and transport of organic contaminants models, K_d is considered to be a function of the fraction of organic carbon for suspended solids or sediments, f_{OC}, and the organic-carbon partition coefficient, K_{OC}:

$$K_d = f_{OC} \cdot K_{OC} \tag{11}$$

Values of K_{OC} and K_{DOC} can be approximated from octanol-water partition coefficients (Karickhoff *et al*., 1979; Chiou *et al*., 1977; Schwarzenbach *et al*., 2003). Chiou *et al*. (1977, 1998) found that for aromatic compounds sorbed in sediments the following correlation could be applied:

$$\log K_{OC} = 0.904 \cdot \log K_{ow} - 0.34 \tag{12}$$

This correlation has been used by Wiberg and Harris (2002) to study the desorption of p,p'-DDE from sediment during resuspension events on the Palos Verdes shelf in California.

According to the best values determined by Pontolillo and Eganhouse (2001) in their review, the octanol-water partitioning coefficients of DDT, DDE and DDD are set to $2.027*10^6$ (Brooke et al 1990), $9.03*10^6$ (de Bruijn et al. 1989) and $1.62*10^6$ (de Bruijn et al. 1989) respectively.

2.2 Air-Water Exchange

The air-water flux ($F_A^{A/W}$, ng·m^{-2}·s^{-1}) assuming equilibrium between the two phases at the interface (*i*) is given by (Westerterp *et al*., 1984) as:

$$F_A^{A/W} = \left(\frac{1}{k_G \cdot K_{GL}} + \frac{1}{k_L} \right)^{-1} \left(\frac{C^{Air}}{K_{GL}} - C^{diss} \right) \tag{13}$$

where C^{diss} and C^{Air} are the gas-phase and the dissolved (liquid) concentrations of A (ng/m^3), respectively, K_{GL} is the dimensionless gas-liquid distribution coefficient, $K_{GL} = C_{AG}^i / C_{AL}^i$, which may be calculated from the Henry's law constant using: $K_{GL} = \frac{H}{R \cdot T}$, and k_G and k_L are the air-water mass transfer coefficients (m/s).

These mass transfer coefficients are normally correlated for many systems by analogy with heat transfer coefficients in terms of hydrodynamic behaviour and physical properties, such as:

$$Sh \propto \mathrm{Re}^{n_1} \cdot Sc^{n_2} \tag{14}$$

where *Sh*, *Re* and *Sc* are the Sherwood, Reynolds and Schmidt numbers respectively, defined as:

$$Sh = \frac{k \cdot d}{D} \tag{15}$$

$$\mathrm{Re} = \frac{d \cdot v \cdot \rho}{\mu} \tag{16}$$

$$Sc = \frac{\mu}{D \cdot \rho} \tag{17}$$

where d and v are a linear dimension and a velocity characterising the dispersion, D is the coefficient of molecular diffusion of the species considered and ρ and μ are the density and viscosity of the fluid.

2.2.1. Liquid side

In the field of air-sea gas exchange several correlations have been developed based on laboratory wind tunnel studies and *in situ* measurements (Liss and Merlivat, 1986; Duce *et al*., 1991). For the case of the liquid phase mass transfer coefficient, k_L, these correlations are normalized to a gas with a Sc = 600, i.e. CO_2 at 20 ^{o} C, and given as function of the wind speed at 10 m height, u_{10} (m/s). In this work we have used a recent correlation developed by Nightingale *et al*., (2000) that has been recently employed to estimate the global dynamics and sinks of organic pollutants by Dachs *et al*. (2002). This correlation can be written as:

$$k_{L\,norm} = 6.667 \cdot 10^{-7} u_{10} + 1.6944 \cdot 10^{-7} u_{10}^2 \tag{18}$$

where k_L is given in m/s. In order to correct for a different Schmidt number one has to modify the value as follows:

$$k_L = k_{L_{norm}} \left(\frac{Sc_A}{600} \right)^{-0.5} \tag{19}$$

a/ *Water viscosity as a function of temperature*

The water viscosity (cP) is calculated using the following correlation:

$$\ln \mu = B \left[\frac{1}{T} - \frac{1}{T_0} \right] \tag{20}$$

where B and T_0 are two constants fitted from experimental data (B = 2.13055·10^3, T_0 = 293.793) and T is in K

b/ *Water density as a function of temperature*

The water density (gr/cm^3) was adjusted as a function of experimental data using a polynomial function:

$$\rho = 0.60721 + 2.8648 \cdot 10^{-3} \mathrm{T} - 5.2225 \cdot 10^{-6} \mathrm{T}^2 \tag{21}$$

where T is the temperature in K.

c/ *DDT, DDE and DDD liquid phase diffusion coefficients as a function of temperature*

For an organic solute diffusing into water the most used correlation is the Wilke and Chang (1955) correlation:

$$D_L = \frac{F \cdot T}{\mu} \tag{22}$$

where T is the temperature of the solvent (K) and μ is its viscosity (cP), and F is given by:

$$F = \frac{7.4 \cdot 10^{-8} (\phi M)^{0.5}}{V_b^{0.6}} \tag{23}$$

and V_b (cm^3/mol) is the molar volume of the organic compound at its normal boiling point, M is the molecular weight (g-mol) of solvent and ϕ is the association factor of the solvent, ϕ=2.6 for organic solutes diffusing into water (Perry and Chilton 1984). D is given in cm^2/s.

The molar volume of DDT, DDE and DDD has been estimated by group contribution method (Perry and Chilton, 1984) and are: 335.41, 312.2 and 314.51 cm^3/mol, respectively. The molecular weights of DDT, DDE and DDD are 354.49, 318.03 and 320.05 g-mol, respectively.

Therefore the liquid diffusion coefficients may be calculated as a function of temperature and water viscosity as:

$$D_L^{DDT}(m^2/s) = 6.85764 \cdot 10^{-12} \frac{T}{\mu_W} \tag{24}$$

$$D_L^{DDE}(m^2/s) = 6.78098 \cdot 10^{-12} \frac{T}{\mu_W} \tag{25}$$

$$D_L^{DDD}(m^2/s) = 6.77246 \cdot 10^{-12} \frac{T}{\mu_W} \tag{26}$$

2.2.2. Gas side

Similarly, several correlations, using water vapour laboratory and field experiments, have been developed to estimate the gas phase mass transfer coefficient (m/s). In this case the normalised value refers to the mass transfer coefficient for water, which may be correlated as a function of wind speed like follows (Schwarzenbach *et al*., 1993):

$$k_G^{H_2O} = 2 \cdot 10^{-3} u_{10} + 3 \cdot 10^{-3} \tag{27}$$

and then

$$k_G = k_G^{H_2O}\left(\frac{D_G^A}{D_G^{H_2O}}\right)^{0.61} \quad (28)$$

where D_G refers to the diffusion coefficients of the chemical and water in the gas phase (air).

Wind speed is important for open water bodies such as lakes and bays. Flowing systems are not significantly affected by winds and hence other type of correlations should be used, see Connolly and Thomann (1985).

a/ DDT, DDE and DDD gas phase diffusion coefficients as a function of temperature

An empirical correlation that has been extensively used to estimate the diffusion coefficients in air is the Fuller et al. (1966):

$$D_G = \frac{10^{-3}\cdot T^{1.75}\left(\frac{M_{Air}+M_B}{M_{Air}\cdot M_B}\right)^{1/2}}{P\left(\left[\sum(\upsilon)_{Air}\right]^{1/3}+\left[\sum(\upsilon)_B\right]^{1/3}\right)^2} \quad (29)$$

where T is the temperature (K), P is the pressure (atm), M are the molecular weights of air (28.8) and the organic compound, and υ are the atomic diffusion values that can be determined form the values in Table 1 ($\Sigma\upsilon_{Air}$=20.1).

Table 1. Atomic diffusion volumes for use in estimating D by the method of Fuller, Schettler and Giddings (1966).

C	16.5	Cl	19.5
H	1.98	S	17.0
O	5.48	Aromatic ring	-20.2
N	5.69	Heterocyclic ring	-20.2

For the specific case of water in air, which is used after to calculate the mass transfer coefficient in the gas phase, we have adjusted the experimental values modifying the atomic diffusion values, i.e. $\Sigma\upsilon_{water}$=10.8.

$$D_G^{H_2O}(m^2/s) = 1.2365\cdot 10^{-9}T^{1.75} \quad (30)$$

For the case of DDT, DDE and DDD it is possible to obtain the following expressions, assuming atmospheric pressure ($\Sigma\upsilon_{DDT}$=92.08, $\Sigma\upsilon_{DDE}$=70.6, $\Sigma\upsilon_{DDD}$=74.56):

$$D_G^{DDT}(m^2/s) = 3.7020\cdot 10^{-10}T^{1.75} \quad (31)$$

$$D_G^{DDE}(m^2/s) = 4.1448\cdot 10^{-10}T^{1.75} \quad (32)$$

$$D_G^{DDD}(m^2/s) = 4.0534\cdot 10^{-10}T^{1.75} \quad (33)$$

b/ The Henry's law constant for DDT, DDE and DDD

The temperature dependence of Henry's law constant can be expressed as:

$$\log H = \log H_{298} + \frac{\Delta H_{vap}}{2.303 \cdot R}\left(\frac{1}{298} - \frac{1}{T}\right) \quad (34)$$

where H_{298} is the Henry's law constant at 25 C (Pa·m^3/mol), ΔH_{vap} is the enthalpy of volatilization from water (kJ/mol), R is the universal gas constant 8.314 10^{-3} kJ/(mol·K) and T is the temperature (K). For DDT ΔH_{vap}=63.5 kJ/mol and H_{298}=1.29 Pa·m^3/mol.

From this equation, the temperature dependence of the Henry's law constant can be expressed as:

$$\log H = A_H - \frac{B_H}{T} \quad (35)$$

Paasivirta *et al*. (1999) give the following valued for DDT, A_H = 13.02, B_H = 3369, for H in Pa·m^3/mol, whereas the use of the definition will give $A_H = \log H_{298} + \Delta H_{vap}/(2.303R298)$, A_H = 11.24 and $B_H = \Delta H_{vap}/2.303R$, B_H = 3316.

For DDE and DDD the following values for Eq. (35) have been reported by Paasivirta *et al*. (1999):

A_H = 12.62, B_H = 3291 , for DDE, and A_H = 12.2, B_H = 3180 for DDD.

2.3 Dry and wet deposition

The dry deposition flux F^d (ng·m^{-2}·s^{-1}) may be estimated from the particle deposition velocity (v_d, m/s) and the micropollutant concentration in the aerosol phase (ng/m^3) as (Swackhamer *et al*., 1999):

$$F_A^d = C_A^{aerosol} \cdot v_d \quad (36)$$

Normal values for particle deposition velocity for lakes and coastal areas usually range from 1·10^{-3} to 8·10^{-3} m/s (Nho-Kim *et al*., 2004). In this work we have used 3.5·10^{-3} m/s as in Van Ry *et al*. (2000).

Wet deposition, F^w may be calculated (Swackhamer *et al*., 1999; Van Ry *et al*., 2000) from the precipitation rate (Pr, m/s) and the micropollutant concentration in rain water (ng/m^3) as:

$$F_A^w = C_A^{rain} \cdot \mathrm{Pr} \quad (37)$$

The sum of both contributions, Eqs. (36)-(37), constitutes the term F^{dep} in Eq. (1).

2.4 Sediment deposition: Settling

Sediments are deposited to the bottom surface through a variety of processes. Gravitational settling is the major deposition mechanism for large sediments (> 1 μm in diameter), whereas for particles smaller then 1μm processes as turbulent diffusion and, for very small particles, Brownian motion start to be important. Typical deposition velocities, w_s, in the submicron range are of the order of 10^{-7} to 10^{-6} m/s. For the gravitational deposition case, the sedimentation rate, w_s (m/s) may be given by the Stokes law, assuming spherical rigid particles:

$$w_s = \left[\frac{g(\rho_p - \rho_w) d_p^2}{18\mu} \right] \tag{38}$$

where g is the acceleration due to gravity (m/s^2), ρ are the densities of the particle and water, respectively (Kg/cm^3), d_p is the particle diameter (m), and μ is the viscosity of water (Kg·s^{-1}·m^{-1}. Corrections to Stokes`s law are required for Reynolds numbers above 0.5 and particles with diameter larger that 100 μm.

However, as summarised by Hawley (1982), observed data collected for settling velocities of lacustrine and marine particles show velocities up to one order of magnitude higher than using the Stokes' velocity. Normally empirical values are used in simulation programs. Typical values are, for example, $3.87 \cdot 10^{-5}$ m/s (Carrer *et al.*, 2000) for the Venice Lagoon, $2.89 \cdot 10^{-5}$ m/s (O'Connor, 1988) or $3.53 \cdot 10^{-5}$ m/s (Farley and Thomann, 1999) for the Hudson River. Callieri (1997) in a study for the Lake Maggiore found significant differences between the inorganic and organic fractions with mean values of $1.74 \cdot 10^{-4}$ m/s and $2.32 \cdot 10^{-5}$ m/s, respectively.

Using these values and the concentration in the particulate phase, Eq. (10), it is possible to calculate the settling flux (ng·m^{-2}·s^{-1}) as:

$$F^{sediment.} = w_s \cdot C^{part} \tag{39}$$

2.5 Sediments-Water Exchange

The adsorption of the chemicals on bottom sediments can significantly affect chemical concentrations in a surface water body. If sediment is saturated with a chemical, removing the chemical from surface water will lead to desorption of the chemical and, therefore, to a decrease in the chemical concentration in water significantly less than if no contaminated sediments were present. Therefore, information on fluxes across the sediment water interface is important when modelling the fate and effects of contaminants.

The flux of a species across the sediment water interface can be calculated with (Portielje and Lijklema, 1999):

$$F^{W/S} = -vC_{sed}^{z=0} + \phi D_{eff,0}\left(\frac{\partial C_{sed}}{\partial z}\right)_{z=0} \quad (40)$$

where v is the rate of infiltration ($v > 0$) or seepage ($v < 0$), i.e. advective flow rate; $D_{eff,0}$ is the effective diffusion coefficient at the sediment-water interface; ϕ the porosity; C_{sed} is the concentration of the chemical compound; and z is the depth into the sediment. The stationary concentration profile can be calculated by solving the mass balance (Portielje and Lijklema, 1999):

$$\frac{\partial C_{sed}}{\partial t} = \frac{\partial\left(\phi_z \cdot D_{eff,z}\frac{\partial C_{sed}}{\partial z}\right)}{\partial z} - v\frac{\partial C_{sed}}{\partial z} - R \quad (41)$$

where R represents the overall reaction rate. Depending on the magnitude of the parameters D_{eff}, v and R the flux across the boundary will be controlled by diffusion, advection or chemical reaction or by a combination of all these processes. The effective diffusion coefficient may be calculated as:

$$D_{eff,z} = D + D_{turb,0}e^{-\alpha z} \quad (42)$$

where D is the molecular diffusion coefficient and D_{turb} is the turbulent component that decays exponentially with depth.

The solution of Eqs. (40)-(42) is a difficult task due mainly to the absence of field experimental data and the fact that laboratory column experiments are not able to reproduce properly the turbulence and therefore they tend to underestimate by one or two orders of magnitude the diffusion coefficient at the interface (Portielje and Lijklema, 1999). For these reasons normally as a first approximation the mass transfer between surface water and sediments may be represented as follows (Farley and Thomann, 1999):

$$F^{W/S} = k_{ws}(C_{sed}^{diss+DOC} - C^{diss+DOC}) \quad (43)$$

where k_{ws} is the pore water (interstitial water) -water column exchange rate coefficient (m/s).

Several empirical correlations have been used trying to correlate the exchange rate coefficient with wind speed and physico-chemical properties of the contaminant. For example Thibodeaux and Becker (1982) developed a correlation for wastewater impoundments:

$$k_{ws} = 0.5.u_w^*.\frac{z_w}{x_w}\left(\frac{z_w.u_w^*}{\mu_w}\right)^{1/4}\left(\frac{122}{MW}\right)^{1/2} \quad (44)$$

where z_w is the average depth of the water body (m); x_w is average wind fetch over the water body (m); u_w^* is water friction velocity (m/s) defined as $[u_{10}(Cd{\cdot}\rho_a/\rho_w)^{1/2}]$; u_{10} is the atmospheric wind velocity at a 10 m height above the water surface (m/h); *MW* is molecular weight of the chemical (g/g·mol); ρ_a is the density of the atmosphere (g/cm^3); ρ_w is the density of the water (g/cm^3); μ_w is the water viscosity (m^2/s); and *Cd* is the drag coefficient. Farley *et al*. (1999) in their studies of PCBs contamination in Hudson river, have used a value approximately two times the molecular diffusivity.

Concerning only the sediment-water diffusive transfer coefficient, Di Toro *et al*. (1981) concluded that the main resistance to mass transfer lies in the sediment and that it is possible to write:

$$k_s = 2.2\cdot 10^{-6}\phi\cdot MW^{-2/3} \quad (45)$$

for k_s in m/s. A typical order of magnitude for k_s is then about $1.2{\cdot}10^{-8}$ –$1.2{\cdot}10^{-7}$ m/s. For the case of DDT, DDE and DDD and assuming a value of 0.75 for the porosity in the sediments we have obtained the following values: $3.3{\cdot}10^{-8}$, $3.6{\cdot}10^{-8}$, $3.5{\cdot}10^{-8}$ m/s, respectively.

2.6 Resuspension and burial

There are several processes that may produce entrainment of sediments to the water column. Waves and currents create fluid motion and the shearing stress exerted by the fluid may be of sufficient intensity to cause erosion and resuspension of the sediment and if the fluid velocity is of sufficient magnitude it may induce horizontal motion of resuspended material. This phenomenon involved the complex field of sediment transport and is normally treated using empirical functions that are functions of sediment characteristics, including the water content of the sediment, its particle-size distribution, mineralogy and organic content as well as the biotic component. Many comprehensive discussions of the dynamics of streams (fluvial) sediment transport have appeared in earlier literature, e.g. Simons and Senturk (1977); Garde and Raju (1977). However, in non fluvial water bodies such as lakes, reservoirs, or estuaries, interactions between sediments and water column cannot be described simply in the same way. In these systems, wind plays an important role as a source of kinetic energy, which, once transferred to the water, generates turbulence-producing waves and currents. The wind induced turbulent kinetic energy influences mixing and

transport processes in the water column. In particular, it controls sediment entrainment from the bed of the water body and its diffusion into the water column, generating a vertical distribution of suspended sediment concentration. The study of this problem is important because of water quality considerations in the presence of contaminated sediment and it has been analysed through laboratory and field experiments, and also through analytical and numerical modelling (e.g. Tsanis and Wu, 1995).

In Chapra (1997) a value for the resuspension velocity is obtained by assuming steady state conditions for the mass balance equation of suspended solids that gives:

$$w_u = \frac{w_s \cdot m}{(1-\phi)\cdot \rho_{sed}} - w_b \tag{46}$$

whereas ρ_{sed} is the sediments density ($2.5.10^6$ g/m^3) and w_b is the burial velocity . The burial velocity in Lake Maggiore has been estimated from sediment dating techniques (CIPAIS 2002) as $1.93 \cdot 10^{-10}$ m/s (mean value).

2.7 Pore water diffusion

The sediments in Lake Maggiore (CIPAIS, 1999b; 2002b; 2003) show a DDT contamination which tends to decrease towards the surface. Thus, there is a gradient of DDT in the pore water and the dissolved contaminant diffuses towards the surface. In order to take into account this effect, we have introduced in the model the pore water diffusion between superficial and depth sediments as:

$$F^{S/S} = \frac{D_L^A}{H}(C_{sed_2}^{diss} - C_{sed_1}^{diss}) \tag{47}$$

where H is the distance between the centre of the two sediment layers.

2.8 Sediment biodiffusion

The biological reworking of sediment by the activity of organisms (bioturbation) causes displacements of particles and pore water. This process can be represented with the biodiffusion equation:

$$F^{bio} = \frac{D_B}{H}\left(C_{sed\,2}^{tot} - C_{sed1}^{tot}\right) \tag{48}$$

where D_B is the biodiffusion coefficient. This parameter is correlated to the burial velocity w_b and can be estimated by means of the empirical relation (Boudreau, 1997):

$$D_B = 15.7 \cdot w_b^{\,0.69} \tag{49}$$

According to Eq. (49), D_B is equal to $3.7\ 10^{-11}$ (s^{-1}).

2.9 Chemical loss rate

There are several mechanisms and reactions responsible for the chemical loss of a contaminant. The more important are: photolysis, hydrolysis and biodegradation.

The photolysis rate of decay depends mainly on the absorption spectrum of the chemical, the incoming solar radiation and its subsequent penetration and attenuation. Normally the process is approximated as a first order reaction (Thomann and Mueller, 1987). During the hydrolysis, the chemical compound reacts with water and, normally, the process is modelled as a second-order reaction rate with dependence on the molar concentrations of $[H^+]$ or $[OH^-]$. Finally during biodegradation the chemical is degraded by bacteria and fungi through metabolic activity. These processes are normally modelled using Monod's type equations with saturation at high rates (Monod, 1950).

These processes, of course, are highly dependent of the specific chemical (or families) compound and, hence, knowledge about its reactivity and biological pathways is necessary before including such reactions in the model.

Specifically for DDT we have considered in the model the transformation to DDE by neutral and basic nucleophilic elimination. In the last case the rate constant depends on pH of the lake but we have assumed a constant value equal to 7. Then the rate constant is $k_{DDE} = 2.5 \cdot 10^{-9}$ (s^{-1}) according to Schwarzenbach *et al*. (2003). DDT may also suffer reductive dechlorination in the sediments to form DDD and the degradation constant is $2.44 \cdot 10^{-9}$ (s^{-1}) (Howard *et al*. 1991). Also, the hydrolysis rate of DDD is set to $7.85 \cdot 10^{-10}$ (s^{-1}) (Kollig 1993).

LAKE MAGGIORE PARAMETERS AND BOUNDARY DATA

Lake Maggiore is the second largest (212 km^2) and deepest (370 m) Italian subalpine lake (Fig.2; Table 2). The lake is located in the foothills of the Alps, just north of the most industrialized part of Italy, which includes cities such as Milan and Turin (Fig. 2). It is situated at 194 m above sea level (a.s.l.), in a fluvial valley reshaped by glacier activity in the Alpine area of Northern Italy, and more precisely in the central part if the Alpine chain, with its western part bordering on the Pennine Alps, and its central-eastern part on Lepontine Alps. This region forms one of the largest basins in Italy, and in any case is the most extensive of the watersheds of lentic waterbodies (Carollo *et al*., 1985) of the national territory (6599 Km^2). It is connected with river Po, the most important watercourse in Italy, through its effluent the Ticino.

The catchment lies half in Italy (Piedmont and Lombardy) and half in Switzerland (Canton Ticino). The northernmost part of the area is occupied by the Alps, with the highest peak (Monte Rosa) 4633 m a.s.l.; most of population (634,000) lives in the subalpine area in the southern part of the catchment where the main industrial activities are also located.

The catchments are almost exclusively formed of granitic and granodioritic rocks. Vegetation occupies most of the catchments as the altitude rises, with coniferous forest covering about 43% of the total surface. Gneisses, mica-schists and para-gneiss are very common, but in the upper part of the catchment basic rocks are also present (Boggero *et al.*, 1996).

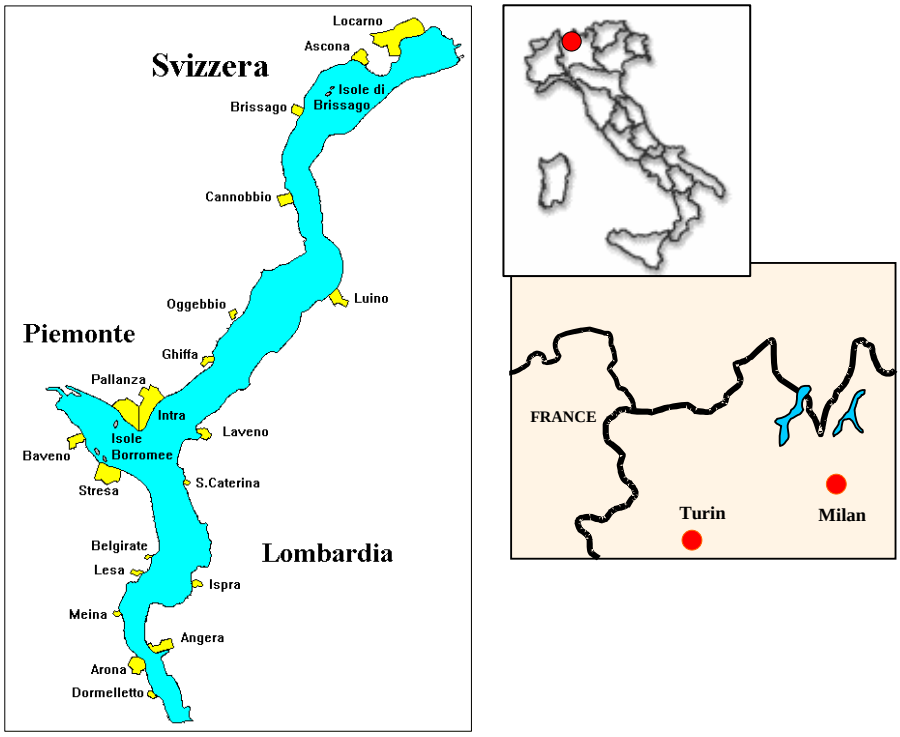

Figure 2. General layout of Lake Maggiore.

Table 2. Main morphometric and hydrological features of Lake Maggiore and its catchment.

Mean watershed altitude	1270 m a.s.l
Mean lake altitude	194 m a.s.l
Watershed area (lake included)	6599 km^2
Lake area	212 km^2
Watershed/lake area	31.1
Mean depth	177 m
Maximum depth	370 m
Theoretical renewal time	4 years

Lake Maggiore is oligotrophic by nature, as testified by early limnological studies (Monti 1929; Baldi 1949) and by analysis of the sedimentary pigments (Guilizzoni *et al*., 1983). However, its status shifted from oligotrophic to mesotrophy in the 70s, then back to oligotrophic, which is the present status (Vollenweider, 1965; Guilizzoni *et al*., 1983; Marchetto *et al*., 2000). The eutrophication process started in the sixties: the algal nutrient concentration in lake water started to increase and was soon followed by an increase of the phytoplancton abundance, biovolume and primary productivity (Ravera and Vollenweider, 1968; Morabito and Pugnetti, 2000). The lake reached a trophic state close to eutrophy in the late seventies, when loads peaked and the maximum in-lake TP concentration at winter mixing was recorded (around 30 $\mu g.l^{-1}$; Mosello and Ruggiu, 1985). From this time, the P loads have been gradually reduced due to different measures: adoption of treatment plants and the reduction of total phosphorous in detergents being the most important. Consequently, the values of TP at winter mixing gradually decreased to values around 10 $\mu g.l^{-1}$ corresponding to the most recent years (Calderoni *et al*., 1997). The slow reversal of the trophic state of Lake Maggiore is documented by many papers: from a biological point of view, strong emphasis was put in the 80s on the apparent resilience of the plankton communities against falling phosphorous (de Benardi *et al*., 1988).

Lake Maggiore has been selected for the development of the contaminants fate model because the lake is one of the most thoroughly investigated lakes in Italy, both concerning physical, chemical and biological aspects, and in terms of the continuity of series of measurements (Istituto Italiano di idrobiologia, Pallanza, http://www.iii.to.cnr.it/).

3.1. General contaminant model parameters

Table 3 summarizes the main parameters used in the mass balance model of Lake Maggiore. The mean monthly values for 1998, obtained from CIPAIS for the precipitation rate, the wind speed, the particulate organic carbon and the dissolved organic carbon have been used for forcing the model during the year. Reported in Table 3 are their mean annual values.

Table 3: Main hydrographic and meteorological parameters of the Lake Maggiore

Parameter	Value
Volume (m^3)	$3.75 \cdot 10^{10}$
Surface (m^2)	$2.1251 \cdot 10^{8}$
Sediment volume (1 cm layer) (m^3)	$2.1251 \cdot 10^{6}$
Mean precipitation rate (m/s)	$6.49 \cdot 10^{-8}$
Mean wind speed (m/s)	0.99
Mean water temperature (°C) (daily data)	13.7
Max. water temperature (°C)	25.8
Min. water temperature (°C)	6.5
Mean air temperature (°C) (monthly data)	12.8
Max. air temperature (°C)	24.0
Min. air temperature (°C)	3
Mean Particulate Organic Carbon (POC, µg/l)	223
Mean Dissolved Organic Carbon (DOC, µg/l)	1099
Sediments porosity	0.75

Concentration of Suspended particulate matter (SPM, mg/l) in Lake Maggiore was measured during the period from March 2003 to January 2004 (Olivella *et al.*, 2004) with a mean value of 0.87 mg/l which agrees with the value obtained using the correlation from Lindström *et al*. (1999) that uses Total Phosphorous concentrations (TP, µg/l):

$$\log(SPM) = 1.56 \log(TP) - 1.69 \qquad (50)$$

Mean TP concentrations in Lake Maggiore are around 11.3 µg/l (CIPAIS, 1999a) which gives 0.90 mg/l as an approximate value for SPM.

3.2. Forcing functions

A first simulation attempt was started using mean annual values for all the parameters. However, the changes in DDT concentrations during the year (CIPAIS, 1999) asked for another approach to be able to model the DDT dynamics. For this reason, it was chosen to consider all available data (monthly values) as forcing values and to assume linear interpolation between these values. Forcing functions are DDT fluxes from the watershed, wet and dry deposition, air concentrations values, rainfall values and wind speed. As mainly data on DDT from the watershed was available for 1998, this was the year chosen to simulate.

3.2.1 *Water flows*

In order to run the model, we have considered runoff fluxes from the main rivers as described in CIPAIS (1999a). The main tributaries in terms of fluxes, as can be see in fig. 3, are the Ticino, Toce and Tresa rivers.

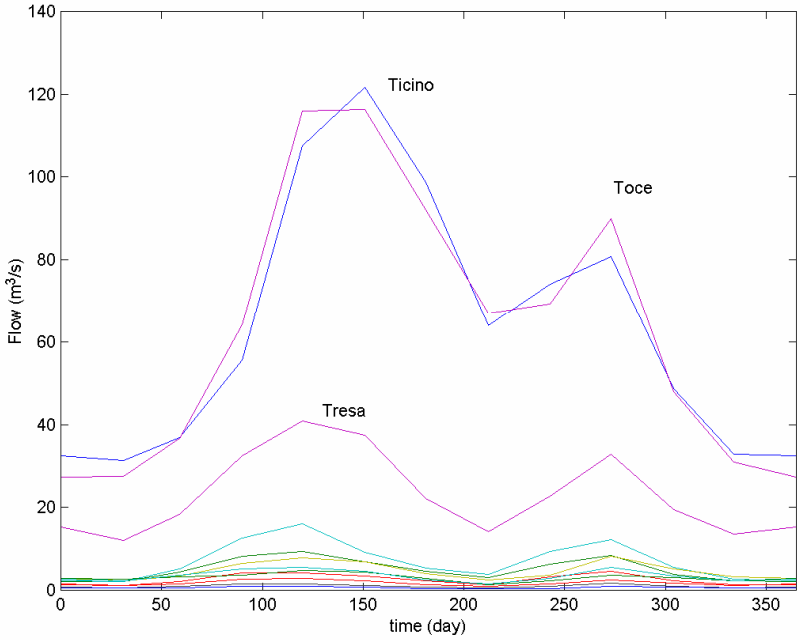

Figure 3. Water flows to Lake Maggiore. Mean monthly values from 1978-1998 (CIPAIS, 1999a).

3.2.2 DDT fluxes

Concerning the input of DDT from the watershed we have considered the data from CIPAIS (1999b), where monthly concentrations of the different DDT isomers and degradation products were measured. Based on these data the total annual DDT input is equal to 4.9 kg y-1. As an example, values for Ticino river inlet are shown in fig. 4.

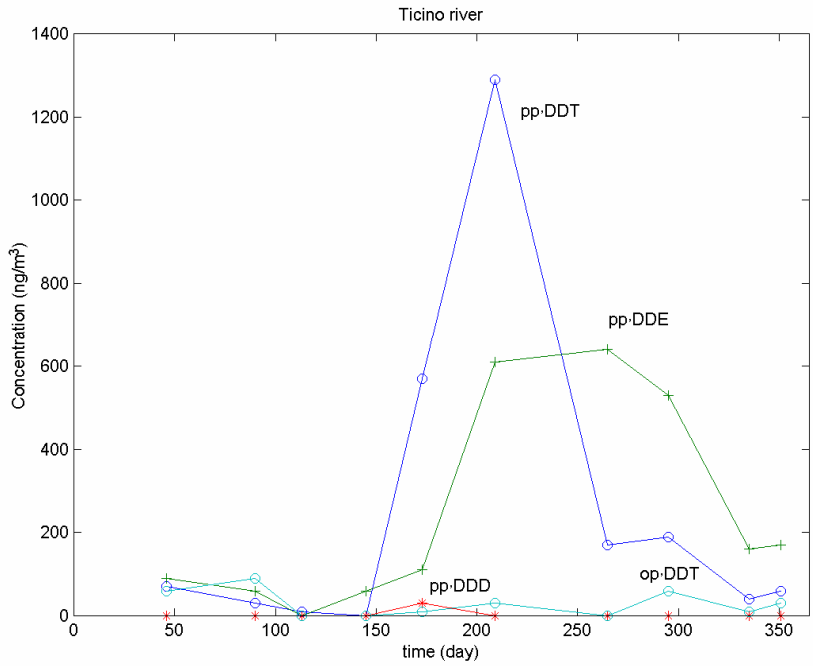

Figure 4. DDT concentrations in 1998 measured in the Ticino river before entering Lake Maggiore (CIPAIS, 1999b).

3.2.3 DDT concentrations in precipitation

Unfortunately, we have been not able to find concentrations data for 1998. However, using data from CIPAIS (2002b) from several stations, i.e. Pallanza, Alpe Devero, Locarno Monti and Robiei collected during 2001 and 2002, we have calculated mean values of DDT concentrations during a hypothetical year. Table 4 represents the monthly mean values obtained.

Table 4. Mean values of total DDT concentration in rain.

	Concentration (ng/m³)											
Compound	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**
p,p'-DDT	240	120	705	593	763	720	285	250	448	788	2053	500
p,p'-DDE	163	160	575	853	1117	113	123	100	138	185	1900	400
p,p'-DDD	157	125	100	88	650	105	158	138	163	125	775	500
o,p'-DDT	133	125	88	150	90	125	138	150	213	125	1543	500
o,p'-DDE	250	125	88	188	83	125	138	113	200	88	1110	500
o,p'-DDD	783	300	238	288	147	200	200	200	300	150	337	160

3.2.4 DDT concentrations in air

Unfortunately, no experimental data was available concerning the DDT concentrations in air (gas + aerosol phases). Therefore, in order to force our model, we decided to use the experimental values of total DDT (DDE and DDD) concentrations in rain to estimate the values of particle associated and air concentrations. The atmospheric concentration of a chemical in the atmosphere may be obtained as (Jurado *et al*., 2004):

$$C_A^{atmosphere} = \frac{C_A^{rain}}{W_T} \tag{51}$$

where W_T is the overall washout ratio that may be estimated as:

$$W_T = W_G(1-\phi) + W_P \cdot \phi \tag{52}$$

where W_G and W_P are the gas and particle washout ratios, respectively, and ϕ (dimensionless) is the fraction of aerosol-bound DDT to total atmospheric DDT concentration, i.e.

$$\phi = \frac{C_A^{aerosol}}{C_A^{aerosol} + C_A^{gas}} \tag{53}$$

The overall washout ratio can be determined from simultaneous measurements of the concentration of DDT in air and in precipitation, and it is assumed to be a function of particle size distribution, particle chemistry, relative humidity and temperature (Scott,

1981). For example, using data from Takase *et al*. (2003) for three sampling sites in Japan, the overall washout ratio, W_T, for p,p'-DDT may be estimated as 5819 ± 1592, whereas using data from Coupe *et al*. (2000), it is possible to derive a overall washout ratio of 8823 for p,p'-DDE and a ϕ value of 0.015. Park *et al*. (2001) obtained by atmospheric monitoring in Galveston Bay at Seabrook, Texas the following mean values for W_T: 2044, 1545, 13828, 2986, 1636, 23367 for p,p'-DDT, p,p'-DDE, p,p'-DDD, o,p'-DDT, o,p'-DDE and o,p'-DDD, respectively. Furthermore, 0.156, 0.04, 0.28, 0.125 and 0.13 for p,p'-DDT, p,p'-DDE, p,p'-DDD, o,p'-DDT and o,p'-DDD, respectively. In a study from Holoubek *et al*. (2004) for an emission inventory of POPs in the Czech Republic mean ϕ values of 0.34, 0.0752 and 0.36 were obtained for p,p'-DDT, p,p'-DDE and p,p'-DDD, respectively. ϕ values may be obtained from gas-particle partitioning models (Pankow, 1994):

$$\phi = \frac{K_p[TSP]}{1 + K_p[TSP]} \tag{54}$$

where K_p is the particle-gas partitioning coefficient (m^3/kg) and [TSP] is the total suspended particle matter (kg/m^3). The particle-gas partitioning coefficient may be obtained from a correlation developed by Finizio *et al*. (1997) based on the octanol-air partition coefficient, K_{oa}, and in the fraction of organic matter, f_{OM}, on the aerosol that is free to exchange chemical:

$$\log K_p = \log K_{oa} + \log f_{OM} - 2.91 \tag{55}$$

Values of K_{oa} may be calculated using the correlation developed by Shoeib and Harner (2002):

$$\log K_{oa} = A + B/T \tag{56}$$

where T is in degrees Kelvin and the parameters are given by the same authors, see Table 5.

Table 5. Parameters for $\log K_{oa} = A + B/T$ (Shoeib and Harner, 2002).

Compound	**A**	**B**	**Temp. range (°C)**
p,p'-DDT	-5.63	4603	5-45
p,p'-DDE	-7.49	5116	5-35
p,p'-DDD	-3.94	4185	5-35
o,p'-DDT	-5.95	4590	5-35

Typical values of f_{OM} and [TSP] for Northern Italy in the pre-Alps – open rural or mountain areas- region are 0.2-0.3 and $30\text{-}50 \cdot 10^{-9}$ kg/m^3 (Braga Marcazzan, 1998),

respectively. An example of the dependence of ϕ on temperature for given values of [TSP] and f_{OM} predicted by applying these correlations is depicted in fig. 5.

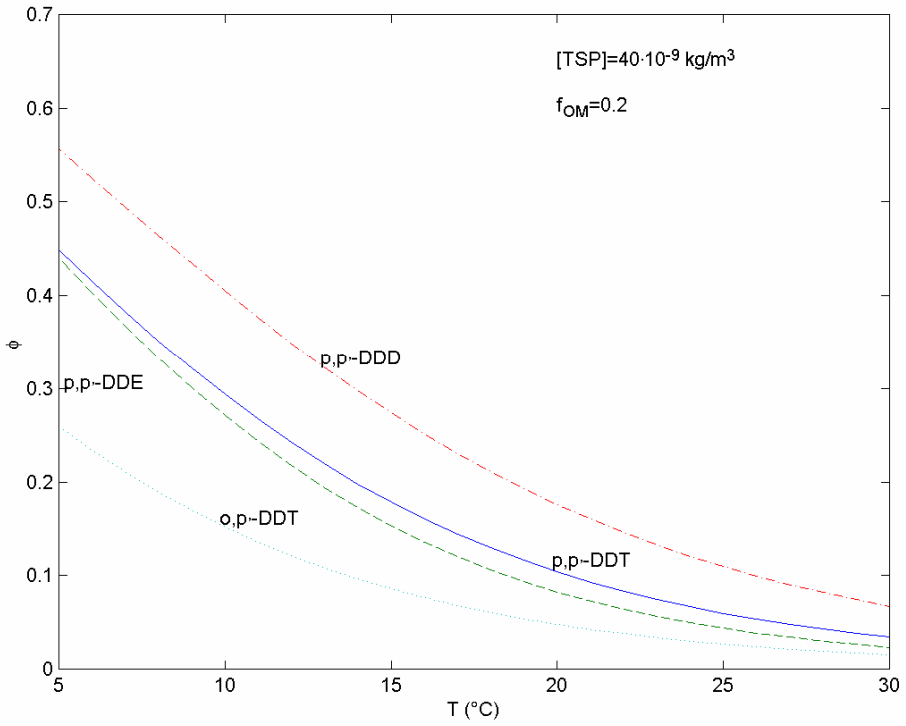

Figure 5. Dependence of fraction of aerosol-bound chemical to total atmospheric chemical concentration for p,p'-DDT, p,p'-DDE, p,p'-DDD and o,p'-DDT

To estimate the distribution of concentrations in the air between gas and aerosol it is necessary, apart from estimating ϕ, obtain values for the gas and particle washout ratios and then apply the following equations:

$$C_A^{gas} = \frac{C_A^{rain}}{\left(W_G + \frac{W_P \cdot \phi}{(1-\phi)}\right)} \tag{57}$$

$$C_A^{aerosol} = C_A^{atmosphere} - C_A^{gas} \tag{58}$$

Originally, the W_G gas washout ratio has been estimated using the Henry's law constant as:

$$W_G = \frac{1}{K_{GL}} = \frac{R \cdot T}{H} \tag{59}$$

However, field measurements of DDT (Takase *et al*., 2003) and other POPs (Simcik, 2004) have found higher values. This has been attributed to the gas-phase semivolatile organic compound (SOC) adsorption to the surface of raindrops (Simcik, 2004) where a corrective term into Eq. (60) to take this effect into account has been proposed:

$$W_G = W_G^{diss} + W_G^{ads} = \frac{R \cdot T}{H} + \frac{6000 \cdot K_{ia}}{d_R} \quad (60)$$

where K_{ia} is the air-water interface absorption constant and d_R is the diameter of raindrops assumed to be spherical. Correlations to estimate K_{ia} use the Junge-Pankow (Pankow, 1987) adsorption model and depend on the sub-cooled liquid vapour pressure (p_L^o). Unfortunately, we have not found such correlations for DDT and related compounds. Therefore, we have used the experimental correction to the Henry's law constant, provided by Takase *et al*. (2003) to take into account this effect. In this case:

$$W_G = \frac{R \cdot T}{H_{corr}} \quad (61)$$

where $\log(H_{corr}) = \log(H_A) + 13.17 - \frac{4023}{T}$.

Reported values for measured particle washout rations, W_P, show a high variability (see Jurado *et al*., 2004 for a review). Due to this high variability that depend on the complexity of the scavenging process and the high variability of meteorological conditions and natural aerosols, Jurado *et al*. (2004) used an average value $2 \cdot 10^5$ for PCBs and PCDD/Fs. This value has been also used by other authors (Mackay *et al*., 1986; Bidleman, 1988) for modelling and calculation exercises. Therefore, we have used it in our work.

3.2.5 DDT initial conditions in sediments

The initial concentration of DDT isomers and degradation products in sediments were defined according to mean concentration measured in sediment cores corresponding to the period just before 1998. These cores were sampled at different locations in the Lake Maggiore (CIPAIS 2002b).

Table 6: Initial concentration of DDT

Compound	Concentration (mg/m^3)
p,p'-DDT	4.63
p,p'-DDE	22.6
p,p'-DDD	21.5
o,p'-DDT	2.71
o,p'-DDE	6.09
o,p'-DDD	13.8

SIMULATION RESULTS

In a first step the model is used to calculate concentrations and fluxes under steady state conditions. Thereafter, the Lake's recovery time is estimated by calculating the half-life decay time of the different DDT compounds.

4.1. Steady-state concentrations

Steady state conditions were obtained by simulating 20 years with constant input coming from the rivers and atmosphere. The concentrations of DDT in the water column were compared to concentrations measured during 1998 in the Ticino Emissario River, which is the effluent of the Lake Maggiore, under assumption that the concentration in the Ticino Emissario represents the mean concentration in the Lake. Fig. 6 shows that the simulation results tend to underestimate the DDT concentrations, except for pp'DDD and op'DDE, but in general they are within the range of the standard deviation. No standard deviation could be calculated for op'DDE since it was measured only once, while for the op'DDD no data were available.

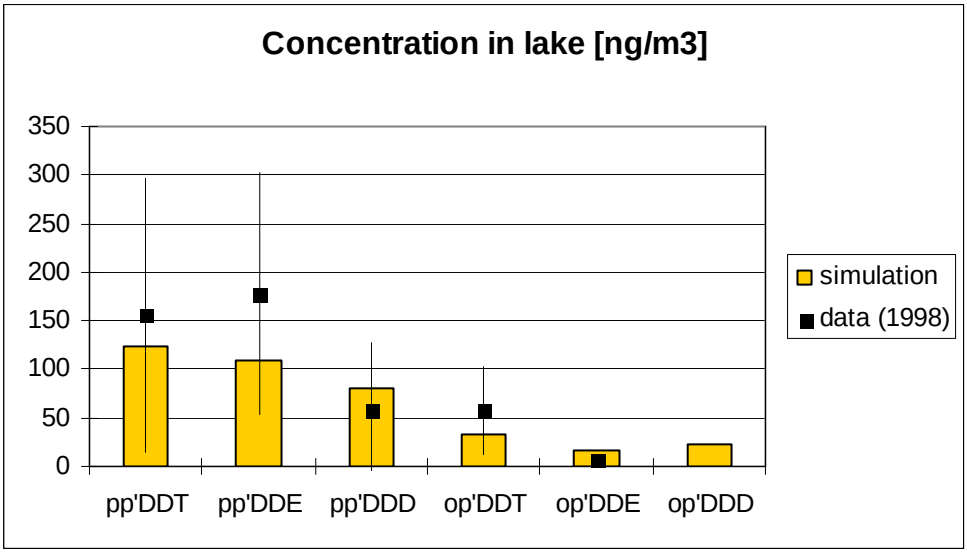

Figure 6. Steady state concentration of the DDT in the water column of Lake Maggiore compared to data of Ticino Emissario measured in 2001 (mean ± standard deviation)

The steady state concentrations of DDT in the sediment were compared to concentrations measured in the surface layer during 2001 (fig.7). The comparison shows a reasonably good overlap, except for pp'DDT where the simulated concentration in much smaller than the measured data.

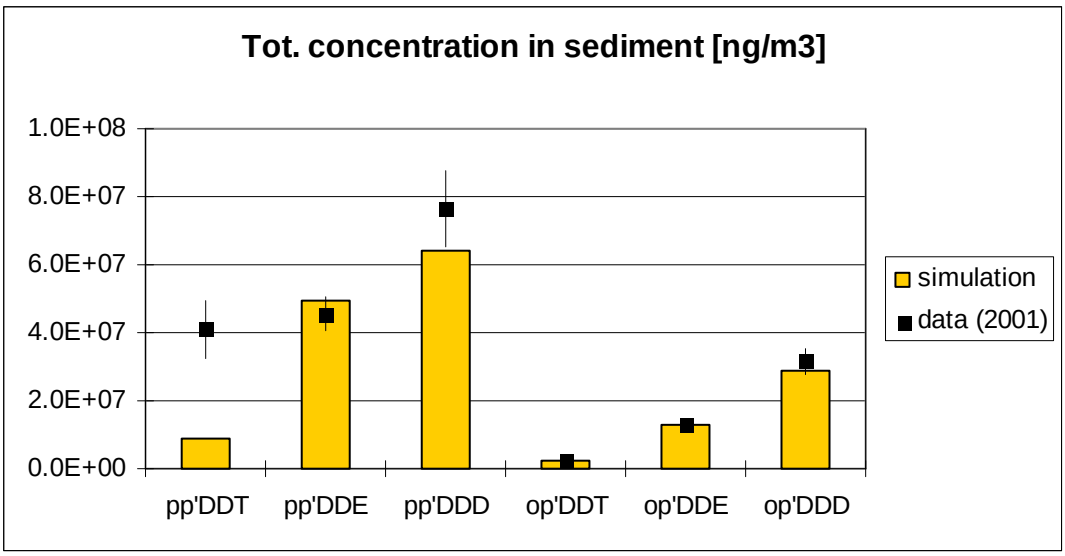

Figure 7. Simulation results of the DDT concentration in the sediments compared with data of 2001 (mean ± standard deviation)

4.2. Annual fluxes

Annual ingoing and outgoing fluxes were calculated for steady state conditions and the results are represented in fig. 8. The air-water exchange flux includes the dry and wet deposition, as well as the gaseous exchange. Sedimentary exchange takes account of the pore water diffusion, the biodiffusion and the burial. Fig. 8 does not explicitly represent the chemical losses due to transformation of DDT to DDE and DDD, nor the hydrolysis of DDD.

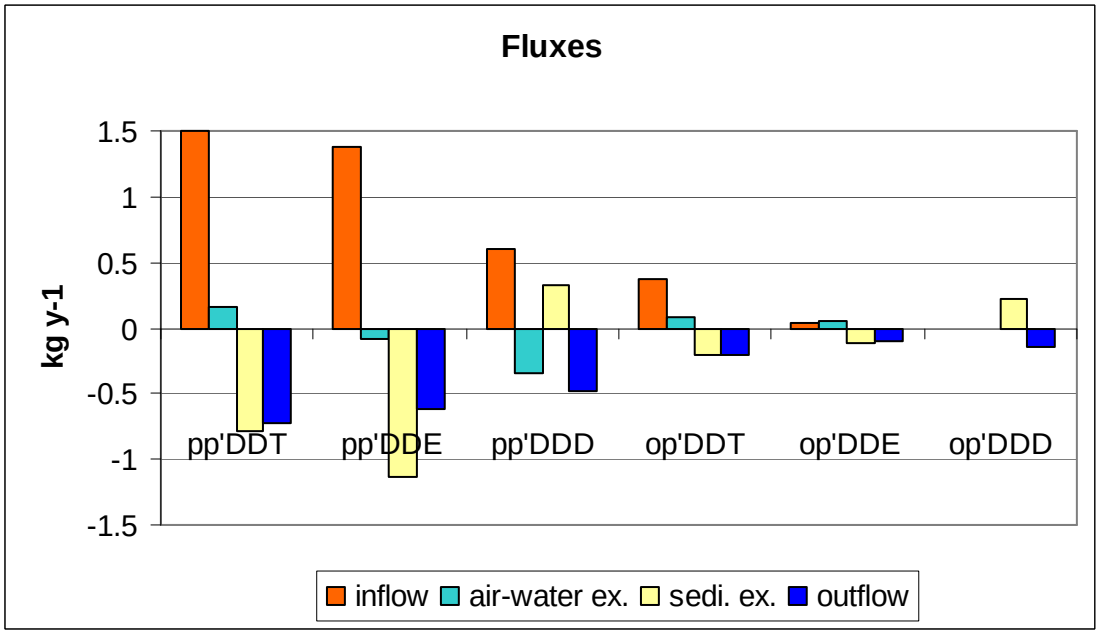

Figure 8. Annual fluxes of DDT into and out of the lake according to steady state simulation

The results show that the sediments are an important trap for DDT and DDE, while for DDD the sedimentary exchange is positive, meaning that the fluxes are upwards from the underlying sediments to the water column. On the other hand, the air-water exchange contributes to the input of pp'DDT, op'DDT and op'DDE into the system, while pp'DDE, pp'DDD and op'DDD are lost to the atmosphere through gaseous exchange.

The CIPAIS (1999b) report estimates a yearly DDT input of 4.9 kg y^{-1}, but according to the forcing function of the model the annual input coming from the tributaries is 3.9 kg y^{-1}. The difference can be explained by the fact that the model does not account for the contribution of the Maggia and the Verzasca rivers because no data were available for their runoff flows. In fact, the contribution of these two rivers is 0.9 kg y^{-1} (CIPAIS 1999b).

4.3. Half-life decay time

A simulation was run to calculate the half-life decay time, i.e. the time it will take until the steady state concentration of the chemical compound will decrease by a half. This time can be calculated assuming exponential decrease:

$$C = C_0 e^{-\lambda \cdot t} \tag{62}$$

where C_0 represents the initial concentration. Assuming $C=C_0/2$ it is possible to obtain:

$$t_{1/2} = \frac{\ln 2}{\lambda} \tag{63}$$

Figure 9 shows the above mentioned simulation for the water column, after the fluxes coming from the watershed, the atmosphere and the sediments have been set to zero, whereas the half-life times have been represented in Table 7.

Table 7. Half-life decay times

Compound	$t_{1/2}$ (d)
p,p'-DDT	591
p,p'-DDE	536
p,p'-DDD	542
o,p'-DDT	591
o,p'-DDE	572
o,p'-DDD	542

The half-life decay times oscillate around 1.5 years. This takes into account the time constant of the lake as well as the chemical transformation of the compounds. The differences between p,p'-DDE and o,p'-DDE are due to the conversion of DDT into

DDE in the water column. In the first case this conversion in less important in relative terms than in the second case.

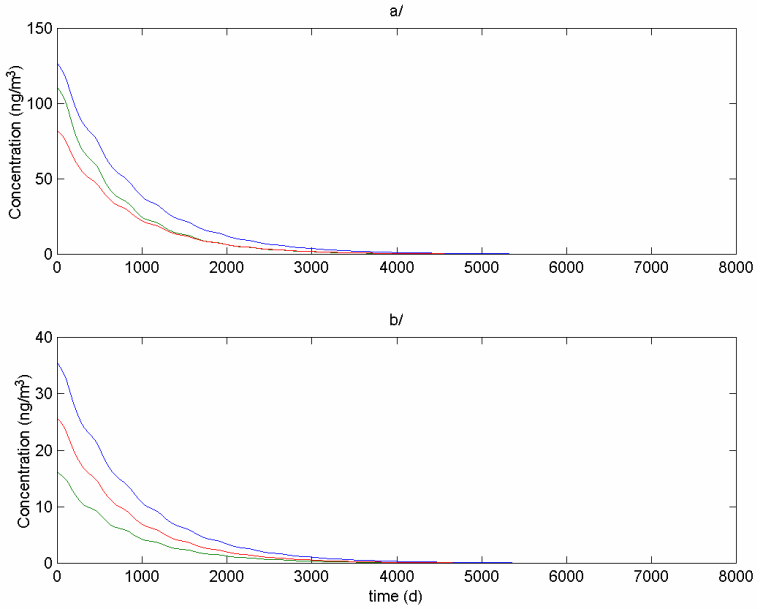

Figure 9. Simulated decay for: a/p,p'-DDT (blue); p,p'-DDE (green);p,p'-DDD (red). b/o,p'-DDT (blue); o,p'-DDE (green);o,p'-DDD (red).

A second simulation has been run assuming that the input from the watershed has disappeared. However, airshed and sediments still exchange DDT and related compounds. As can be seen in fig. 10, this time the concentrations does not reach a zero value. This is due to the atmospheric inputs as well as to the input from the sediments. In one case, o,p'-DDD there is no change in the concentration since for this compound the influence of inputs from watershed is negligible.

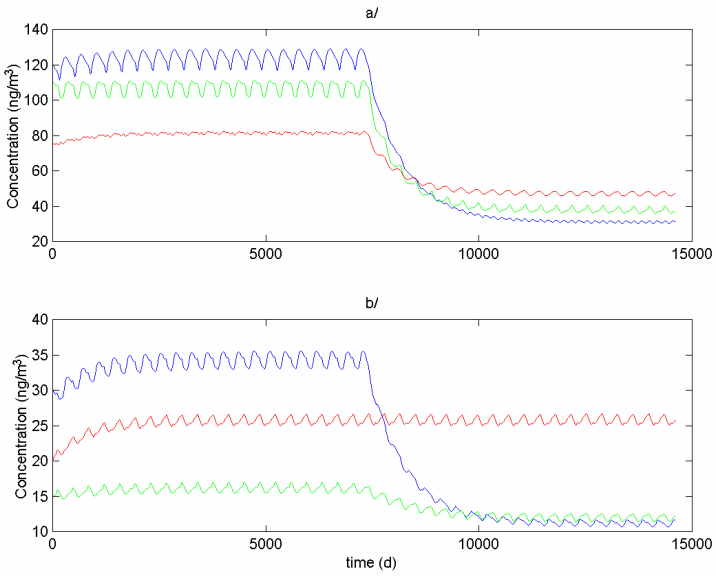

Figure 10. Simulated decay for: a/p,p'-DDT (blue); p,p'-DDE (green);p,p'-DDD (red). b/o,p'-DDT (blue); o,p'-DDE (green);o,p'-DDD (red) after there is no more inputs from the watershed.

CONCLUSIONS

A dynamic mass balance model for p,p'-DDT, p,p'-DDE , pp'-DDD, o,p'-DDT, o,p'-DDE and o,p'-DDD in Lake Maggiore has been developed and validated against experimental data in the water column as well as in the sediments. The obtained values are in general good agreement with experimental measurements and the model is able to simulate with good agreement mean values concentrations in the lake and in the sediments compartments. An annual balance of these compounds has been also carried out. Unfortunately, due to the absence of all forcing data sets for a whole year, the model cannot be properly validated. A more complete data set would be necessary to calibrate it. Furthermore, it has not been possible to find relevant information on the atmospheric compartment in terms of concentrations in gas and aerosol phases.

The fate of a contaminant in the environment is mainly controlled by its physico-chemical properties, thus an accurate determination of those as well as the associated errors would allow a critical assessment of the model uncertainties. Even though DDT and its related compounds, ie. DDE and DDD, have a long history and there are a lot of publications concerning their properties, Pontillo and Eganhouse (2001) has evidenced that we are still far away of having a database of physico-chemical properties able to allow such as assessment. In fact they found that the original data on solubility and octanol-water partition coefficient span 2-4 orders of magnitude and that there is little indication that the uncertainty in these properties has declined over the last 5 decades. They concluded also that if this is the case for DDT, one should expect similar errors in the literature of contaminants, which in turn would probably lead to incorrect environmental risk assessment. A preliminary sensitivity analysis (not reported here) has also evidenced this problem since the final concentrations in the different model compartments are heavily influenced by the physico-chemical properties of a said compound.

Finally, even though a 0D model is able to capture the average values in the water column as well as in the sediments and allow a preliminary calculation of the fluxes between the model's compartments; the high heterogeneity of experimental data calls for the application of a 3D hydrodynamic model of the lake. However, considering that our main interest consists on the coupling with the ecological model developed for Lake Maggiore (Olivella *et al.*, 2003) to analyse the effects of DDT bioaccumulation in its food web chain and to compare with available experimental results (CIPAIS, 1999b; 2002b; 2003), the approach seems adequate.

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European Commission

EUR 21663 EN – DG Joint Research Centre, Institute for Environment and Sustainability
Luxembourg: Office for Official Publications of the European Communities
2005 – 37 pp. – 21 x 29.5 cm
Scientific and Technical Research series

Abstract

Release of chemical substances significantly impacts European waters. Impacts are both direct and indirect, through degradation products, acute and/or chronic toxicity, and/or long-term effects via bioaccumulation in aquatic food chains. As the number of substances is large and measures to reduce emission are costly and time demanding, there is a necessary prioritisation of the efforts through risk assessment studies requiring exposure data, which are both scarce and difficult to obtain. This is complicated by the fact that contaminants may reach the aquatic environment and hence biota and sediments, through several routes ranging from atmospheric deposition (airshed), diffuse and/or point sources in the watershed. Furthermore, a contaminant may arrive constantly during the year or in a pulse due to an accidental release or periodically driven by environmental fluctuations. For these reasons, as a first step, we have developed a model to simulate the fate of DDT family, i.e. pp'DDT, pp'DDD, pp'DDE, op'DDT, op'DDD, op'DDE, in Lake Maggiore. The model is 0D and consists on a dynamic mass balance that includes a time-variable chemical transport and fate model for calculating DDT concentrations in the water column as well as and in sediments.

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